

~~11~~ A11

(12) UK Patent Application (19) GB (11) 2 164 636 A

(43) Application published 26 Mar 1986

(21) Application No 8521151

(22) Date of filing 23 Aug 1985

(30) Priority data

(31) 8421603

(32) 24 Aug 1984

(33) GB

(71) Applicant

The British Petroleum Company Plc (United Kingdom),  
Britannic House, Moor Lane, London EC2Y 9BU

(72) Inventors

Paul Arthur Diddams,  
William Jones,  
John Meurig Thomas

(74) Agent and/or Address for Service

R. F. Fawcett, BP International Limited, Patents Division,  
Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN

(51) INT CL<sup>4</sup>

C01B 33/26

(52) Domestic classification

C1A 13 423 424 D31 D41 G12 G12D31 G12D41 G13 G47  
G47D31 G48 G48D31 G4 G50 G50D31 M10 N13 N47  
N48 N4 N50 PB5 PC VG1  
U1S 1345 C1A

(56) Documents cited

GB A 2031395

GB 1359367

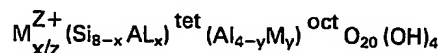
(58) Field of search

C1A

(54) Synthetic smectites and their stabilised pillared analogues

(57) The invention provides synthetic beidellite-smectites (I), their preparation by hydrothermal crystallisation, their pillared analogues, processes for the preparation of the pillared analogues and use of the smectites as catalysts in reactions capable of catalysis by protons.

The synthetic smectites (I) have the formula



wherein  $M^{2+}$  represents exchangeable cations such as  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $x$  has a value of  $0.65 \pm 0.10$ .

The preparation of (I) involves hydrothermal crystallisation of an aqueous gel containing sources of silica, alumina and  $M^{2+}$  in a weight ratio of Si:Al:M of 7-8: 3.5-5: 0:0.5-1.

BEST AVAILABLE COPY

GB 2 164 636 A

FIG.1.1

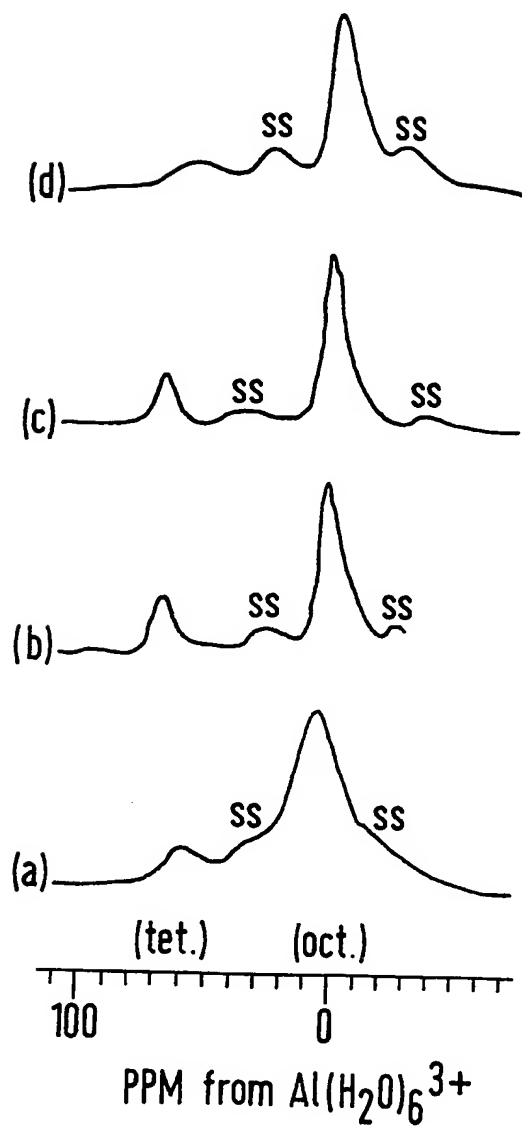
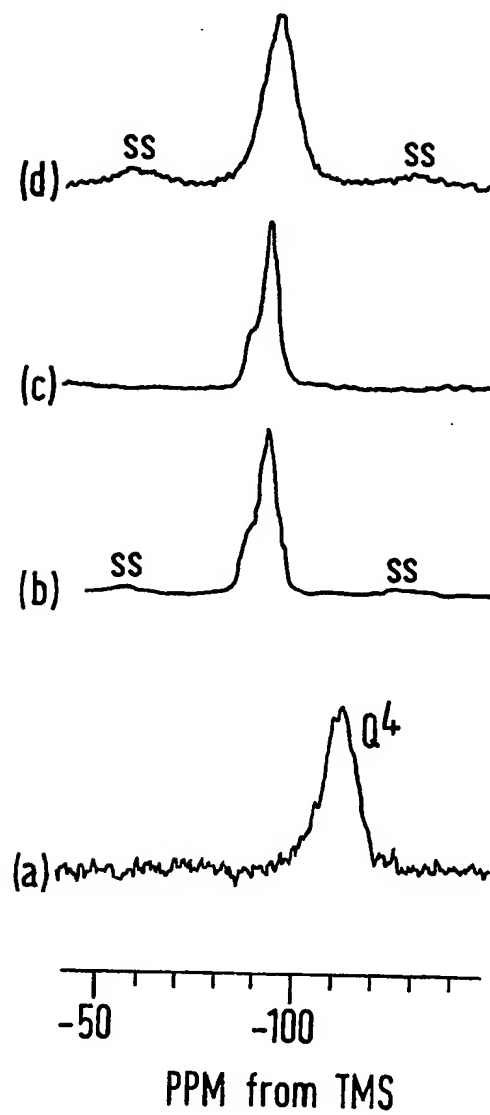


FIG.1.2

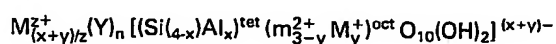
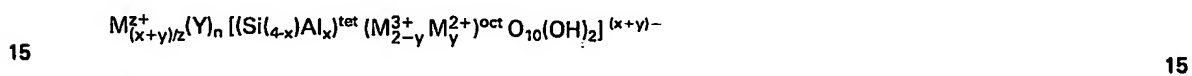


## SPECIFICATION

## Novel synthetic smectites and their stabilised pillared analogues

- 5 The present invention relates to novel synthetic beidellite-smectites, their stabilised pillared analogues, processes for their preparation and their use as catalysts. 5

Smectites are a group of clay minerals of the three-layer sheet type in which the sheet structures are composed of successive layers of tetrahedral silica, octahedral alumina and tetrahedral silica (TOT). The central layer of each sheet (O-layer) may be dioctahedral or trioctahedral. The smectite group of clays is now generally agreed to be classifiable in two sub-groups, i.e. (a) the montmorillonites and (b) the beidellites. This sub-classification derives from a general representation as follows: 10



- 20 where  $M^{z+} (x+y)/z$  represents intercalated (balancing) cations, Y represents water/or other swelling liquid), the square bracket describes the silicate layer, x represents the number of gram atoms of  $Si^{4+}$  replaced by  $Al^{3+}$  in the tetrahedral layers and y represents the corresponding replacement of  $M_{II}^{3+}$  by  $M^{2+}$  or of  $M_I^{2+}$  by  $M^{+}$  in the central octahedral layer of the three layer T-O-T sheet. Smectites are those clays having  $x+y = 0.25$  to 0.60; for sub-group montmorillonite y is very much greater than x and for sub-group beidellite x is very much greater than y. reactions, see for example J.M. Thomas in "Intercalation Chemistry" edited by M.S. Whittingham and A.J. Jacobson, Academic Press, New York, (1982) pp 56-92; J.A. "Ballantine, J.H. Purnell and J.M. Thomas, *Clay Minerals* (1983), 18, 347; EP-A-31252; EP-A-31687; U.S. Patents Nos. 3,962,361, 3,965,043, 3,979,331, 4,238,364 and 4,348,739. Apart from their intrinsic lack of good crystalline order, naturally occurring sheet silicates also tend to contain a variety of paramagnetic impurities which can frustrate attempts to more fully characterise the components that make up the individual aluminosilicate sheets or the pillars that can be introduced to improve the thermal stability of these catalysts. Thus Nuclear Magnetic Resonance (NMR), which is also invaluable for monitoring the course of interlamellar catalysed reactions, can be employed only with a few "high-purity" natural clays, or with commercially available synthetic fluorohectorites that are not well crystallised. 30

- 35 It is an object of the present invention to synthesise and characterise relatively well-ordered smectite-type sheet silicates and to utilise them as catalysts in organic reactions. The objective is fulfilled by the present invention. 35

Accordingly the present invention provides a synthetic beidellite-smectite having the idealised formula:



- wherein  $M_{x/z}^{z+}$  represents exchangeable cations, and 45  
x represents the number of gram atoms of  $Si^{4+}$  replaced by  $Al^{3+}$  in the tetrahedral layers and has the value of  $0.65 \pm 0.10$ . 45

In the synthetic beidellitic-smectite as initially crystallised the exchangeable cations may suitably be magnesium, calcium or a mixture thereof and is preferably magnesium.

- The synthetic beidellitic-smectite may be further characterised by a cation-exchange capacity of  $109 \pm 8$  meq. per 100g of the dehydrated form, corresponding to a layer charge per formula unit of  $0.78 \pm 0.06$  and an interlamellar distance of about 10.0 Angstrom after dehydration at  $150^\circ C$  of the as-prepared magnesium-exchanged material. 50

- The original cations of the as-prepared synthetic beidellitic-smectite may be cation-exchanged using conventional cation-exchange techniques with other suitable cations. Suitable cations include hydrogen ions, ammonium ions and metal cations, for example aluminium, chromium, nickel, cobalt, iron, copper, gallium and vanadium. 55

The synthetic beidellitic-smectite having the formula (I) may suitably be prepared by hydrothermal crystallisation from an aqueous gel containing a source of silica, a source of alumina and a source of the exchangeable cation  $M^{z+}$  in a weight ratio of Si:Al:M of 7 to 8:3.5 to 5:0.5 to 1.

- 60 Suitable sources of silica include, for example, silica hydrosol, silica gel, silica sol and silicic acid. A preferred source of silica is an aqueous colloidal dispersion of silica particles. 60

- Suitable sources of alumina include, for example aluminium chloride, aluminium nitrate and aluminium isopropoxide. A preferred source of alumina is aluminium isopropoxide. It will be appreciated that each source of silica and alumina can be supplied by one or more initial reactants and may be mixed in any order, although it is preferred to add silica last to increase homogeneity. Crystallisation may suitably be effected at 65

a temperature in the range from 100 to 350°C, preferably from 285 to 300°C. The pressure may suitably be autogenous pressure, that is the pressure generated within a closed vessel at the crystallisation temperature, though higher or lower pressures may be employed if desired. The crystallisation period will depend on a number of factors, including the composition of the gel and the crystallisation temperature. Suitably this

5 period may be up to 7 days.

A preferred method of preparing a beidellitic-smectite comprises the steps of:

(A) hydrolysing a hydrolysable aluminium compound,

(B) adding a source of  $M^{2+}$  to the hydrolysate obtained in step (A) and homogenising the mixture

so-obtained,

10 (C) adding sodium hydroxide to precipitate a mixed hydroxide,

(D) separating insoluble matter from the mixture obtained in step (B) and washing until substantially free from extraneous matter,

(E) re-dispersing in water insoluble matter separated in step (C),

(F) adding a source of silica and homogenising the mixture, and

15 (G) crystallising a beidellitic-smectite from the mixture of step (E).

Suitable hydrolysable aluminium compounds include aluminium alkoxides, for example aluminium triisopropoxide. Suitable sources of  $M^{2+}$  include the halide salt, for example the chloride.

In another aspect the present invention provides a stabilised pillared analogue of the synthetic beidellitic-smectite as hereinbefore described.

20 The stabilised pillared analogue may suitably be produced by the process as described and claimed in U.S. Patent No. 4,176,090, i.e. by (a) reacting a smectite with a mixture of a polymeric cationic hydroxy inorganic

metal complex selected from the group comprising aluminium and zirconium complexes and mixtures thereof and water to obtain a smectite having greater than 50% of its surface area in pores of less than 30 Angstroms in diameter after dehydration; and (b) separating the interlayered smectite from the mixture. The

25 reader is referred to this patent for further details of the process.

The stabilised pillared analogue may also suitably be produced by the improved process as described and claimed in USP 4,248,739, i.e. by reacting a smectite with a polymeric cationic hydroxy inorganic metal complex or copolymer thereof having a molecular weight in excess of from about 2,000 to about 20,000 which is prepared by any of the following techniques:

30 (i) heating an aqueous solution of a polymeric cationic hydroxy inorganic metal complex having an initial molecular weight of about 500 to 1200 at a temperature of from about 50°C to 100°C, preferably 80°C, for a period of from 0.1 to 24 hours, typically 1 hour, or

(ii) reacting a polymeric cationic hydroxy zirconium complex having an initial molecular weight of from about 600 to 1200 at a pH of from about 0.5 to 2.0 for about 0.1 to 24 hours, or

35 (iii) reacting a polymeric cationic hydroxy aluminium complex having an initial molecular weight of from about 600 to 1200 at a pH of from about 3.5 to 6 for about 0.1 to 24 hours.

Further details of this process may be found in the aforesaid U.S. Patent No. 4,248,739 which is incorporated herein by reference.

40 The stabilised pillared analogue may also be prepared by the process described and claimed in USP 4,238,364, i.e. by preparing an acidic form of the synthetic beidellitic-smectite as hereinbefore described including ions selected from the group consisting of hydrogen, cerium, gadolinium, lanthanum, neodymium, praseodymium, and samarium; cross-linking the acidic form with oligomeric species of aluminium hydroxide and stabilising the cross-linked acidic form of the smectite. Further details of this process may be found in the aforesaid U.S. Patent No. 4,238,364.

45 Another method of preparing stabilised pillared analogues of the synthetic beidellitic-smectite is described and claimed in US Patent No. 4,216,188, which is incorporated herein by reference.

All the aforesaid methods for producing the analogues rely upon ion-exchange of an exchangeable cation of the clay with a hydroxy polymeric cationic species. In a further alternative the stabilised pillared analogue may be produced by reacting under substantially anhydrous conditions in an organic solvent the synthetic

50 beidellitic-smectite with a material capable of reacting with hydroxyl groups associated with the structure of the smectite so as to interpose a residue of the material between adjacent layers of the smectite. Further details of this process may be found in our published European application No. 0130055 (BP Case No. 5612) to which the reader is referred for further details.

55 As an alternative, or in addition, to cation-exchanging the synthetic beidellitic-smectite, exchangeable cations of the stabilised pillared analogue may be exchanged if so desired.

Both the synthetic beidellitic-smectite and its stabilised pillared analogue may be used as a catalyst or a catalyst support in organic reactions. Examples of organic reactions in which the materials may be used as catalysts include:

(a) a process for the production of an ether by reacting either an olefin or an olefin oxide with an alcohol,

60 (b) a process for the production of an ether by conversion of either a primary or secondary aliphatic alcohol, a polyol or an olefin oxide,

(c) a process for the production of an alkyl aromatic compound by reacting the aromatic compound with either an alcohol or an olefin,

(d) a process for the production of an alcohol by reacting an olefin with water, and

(e) a process for the production of an ester by reacting either an olefin or an olefin oxide with a carboxylic acid.

Further details regarding reactants, reaction conditions and other matters for the reactions (a) to (e) may be found in our European patent publication No 83970 (BP Case No. 5306) which is incorporated herein by reference. The aforesaid reactions are specific examples of reactions which are capable of catalysis by protons, for which the materials of the present invention are applicable as catalysts.

The invention will now be further illustrated by reference to the following Examples.

#### Example 1

##### 10 Preparation of synthetic beidellitic-smectite

The gel is prepared as follows:

Aluminium triisopropoxide ( $\text{Al}(\text{OCH}(\text{CH}_3)_2)_3$ ; 22.73g) was dissolved in 0.1M aqueous NaOH ( $100\text{cm}^3$ ) and the solution was refluxed for 2 hours. Magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; 3.23g) was added and the mixture stirred until uniform. The mixture was centrifuged and washed with deionised water until free of  $\text{Na}^+$ ,  $\text{Cl}^-$  and isopropanol. The solid material so-obtained was re-dispersed in deionised water.

Into the aqueous gel as described above,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  were mixed in the molar ratios 16:3.5:1. The gel was crystallised and from time to time during the crystallisation samples were taken for analyses. A crystalline product was obtained.

X-ray diffraction (of the samples taken at various stages in the crystallisation),  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MASNMR (Magic Angle Spinning NMR), IR, thermal gravimetric analysis (TGA), chemical analysis and analytical electron microscopy showed that a di-octahedral smectite was formed with only Al present in the octahedral sheet and the Mg present as exchangeable cations.

Its cation-exchange capacity was determined as  $109 \pm 8$  meq. per 100g of the dehydrated form, corresponding to a layer charge per formula unit of  $0.78 \pm 0.06$ .

Its surface area (determined by the  $\text{N}_2$ BET method) was  $153 \pm 5\text{m}^2\text{g}^{-1}$ .

The interlamellar distance after dehydration at  $150^\circ\text{C}$  was 10.0 Angstroms.

The identification of the smectite as beidellite was confirmed by the fact that the smectite product could still be expanded (from ca 15.0 Angstroms to 17.2 Angstroms on treatment with glycerol) after the  $\text{Li}^+$ -exchanged form was heated at  $250^\circ\text{C}$  for 12h, cf D.M.C. MacEwan in "The X-ray Identification and Crystal Structures of Clay Minerals" (ed G. Brown), Mineralogical Society, London, 1961, p190.

#### Example 2

Aluminium nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ; 46.52g) and magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ; 3.97g) were dissolved in deionised water at  $80^\circ\text{C}$ . Silica sol (30% aqueous; 49.6g) was added and the mixture was stirred until uniform. It was then evaporated to dryness. The solid composition so-obtained was calcined at  $700^\circ\text{C}$  for the purpose of decomposing the nitrates to the oxides. The resulting amorphous (to X-rays) mixed oxides were finely ground and re-dispersed in deionised water.

The resulting gel (mole ratio of Si:Al:Mg of 8:4:0.5) was charged to an autoclave and heated for 5 days at  $300^\circ\text{C}$  and 1250 psi. A beidellitic-smectite was recovered by centrifuging.

#### Example 3

The procedure of Example 2 was repeated using:

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (46.52g)

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  ( 3.66g), and

$\text{SiO}_2$  (30% aq) (49.6g)

to give a gel in which the mole ratio of Si:Al:Ca was 8:4:0.5.

A beidellitic-smectite was recovered.

#### Example 4

The procedure of Example 2 was repeated using:

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (46.52g)

$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (3.18g)

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1.25g)

$\text{SiO}_2$  (30% aq) (49.6g)

to give a gel in which the mole ratio of Si:Al:Mg:Fe was 8:4:0.4:0.1.

A beidellitic-smectite was recovered.

#### Example 5

The procedure of Example 2 was repeated using:

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (46.52g)

$\text{NaNO}_3$  (2.64g)

$\text{SiO}_2$  (30% aq) (49.6g)

to give a gel in which the mole ratio of Si:Al:Na was 8:4:1.

A beidellitic-smectite was recovered.

**Example 6**

The procedure of Example 2 was repeated using:

Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (34.89g)

Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (7.94g)

5 NaOH (1.24g)

SiO<sub>2</sub> (30% aq) (49.6g)

to give a gel in which the mole ratio of Si:Al:Mg:Na was 8:3:1:1.

A beidellitic-smectite was recovered.

**Example 7**

Aluminium chloride (AlCl<sub>3</sub>·6H<sub>2</sub>O; 46g) and magnesium chloride (MgCl<sub>2</sub>·6H<sub>2</sub>O; 9.65g) were dissolved in deionised water. The solution was heated to 80°C and SiO<sub>2</sub> (30% aqueous) (66.7g) was added and the mixture was stirred until uniform. Thereafter, 35% aqueous NH<sub>3</sub> (65cm<sup>3</sup>) was added to precipitate the mixed hydroxides. The mixture was filtered and washed with deionised water until chloride-free. The mixture was

15 then re-dispersed in deionised water (400ml). The mole ratio of Si:Al:Mg:Na in the gel was 7:4:1:1.

The gel was charged to an autoclave and heated for 3 days at 300°C, 1250 psi. A beidellitic-smectite was recovered.

**Example 8**

20 The procedure of Example 7 was repeated using the following:

CuF<sub>2</sub> (3.76g)

AlCl<sub>3</sub>·6H<sub>2</sub>O (35.4g)

NaOH (1.2g)

SiO<sub>2</sub> (30% aq) (52.5g)

25 to give a gel in which the mole ratio of Si:Al:Ca:Na was 7:4:1:1.

**Example 9**

*Preparation of stabilised pillared analogue of the beidellitic-smectite obtained in Example 1*

The Na<sup>+</sup>-exchanged form of the beidellitic-smectite obtained in Example 1 was treated with the

30 multinuclear cation [Al<sub>13</sub>O<sub>4</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>7+</sup>, generated from chlorhydrol by the method described in US Patent No. 4,176,090 (D.E.W. Vaughan et al) and by J.M. Thomas, Proc. 8th Intl. Congr. on Catalysis, Berlin, July 1984, Vol. 1, p31. The product was calcined at 500°C.

**NMR studies**

35 The <sup>27</sup>Al and <sup>29</sup>Si MASNMR spectra of

(a) dried gel precursor used for synthesis (Example 1),

(b) Na<sup>+</sup>-exchanged synthetic beidellite of Example 1,

(c) Al<sup>3+</sup>-exchanged synthetic beidellite of (b), and

40 (d) Al-pillared analogue of (b) are given in Figures 1.1 and 1.2 respectively. The spectra are referred to free Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> (for <sup>27</sup>Al) (Figure 1.1) and to tetramethylsilane (<sup>29</sup>Si) (Figure 1.2). Peaks labelled SS are spinning side-bands. The precursor gel is seen to contain its silicon predominantly in Si(OSi)<sub>4</sub> environments (Q4), but some Si(OSi)<sub>3</sub>(OAl) cannot be ruled out.

Some tetrahedrally as well as octahedrally coordinated Al, readily distinguished in <sup>27</sup>Al NMR studies [cf. C.A. Fyfe, J.M. Thomas, J. Klinowski and G.C. Gobbi, *Angew Chemie*, 22, 259 (1983) and J.M. Thomas, C.A. Fyfe, J. Klinowski, G.C. Gobbi and M.W. Anderson, A.C.S. Monograph (Symp., Ser) No. 218, 159 (1983)] exists

45 in the gel precursor, and the presence of the tetrahedrally co-ordinated Al in the beidellite product of Example 1 is beyond dispute (see peaks at ca 70 ppm with respect to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>, Figure 1.1 (b) and (c)). The pronounced extra shoulder in the octahedral Al signal obtained from the Al<sup>3+</sup>-exchanged form of the product of Example 1 (Figure 1.1 (c)) is attributed to the mobile interlamellar cations, an assignment confirmed by

50 NMR experiments on static samples. There appear to be at least two types of tetrahedrally bonded Al sites in the pillared beidellite of Example 2 (see region from 55 to 75 ppm in Figure 1.1 (d)).

In view of the well-known problems associated with obtaining quantitatively reliable ratios of (Al)<sup>tet</sup>/(Al)<sup>oct</sup> from <sup>27</sup>Al MASNMR spectra [cf K.F.M.G.J. Scholle, A.P.M. Kentgens, P. Frenken and W.S. Veeman, *J. Phys. Chem.*, 88, 5 (1983)] no attempt was made to establish empirical formulae by this method.

55 The <sup>29</sup>Si MASNMR spectra (Figure 1.2) were, in contrast, of considerable value in estimating the Si/Al ratios in the tetrahedral manifold of the beidellite. Using a variant (cf J.M. Serratosa, J. Sanz et al, *J. Molec. Catalysis* (1984) (27,255) D.T.B. Tennakoon, W. Jones, J.M. Thomas, L.J. Williamson, J.A. Ballantine and J.H., Purnell, *Pro. Indian Acad. (Chem. Sci.)*, 1983, 92, 27) of the equation (cf J. Klinowski, S. Ramdas, J.M. Thomas, C.A. Fyfe and J.S. Hartman, *J. Chem. Soc. Faraday Trans II*, 78, 1025 (1982); S. Ramdas, J.M.

60 Thomas, J. Klinowski, C.A. Fyfe and J.S. Hartman, *Nature*, 292, 228 (1981); G. Engelhardt, U. Lohse, E. Lipmaa, M. Tarmak and M. Magi, *Z. Anorg. Allg. Chem.*, 482, 1981), based on Leowenstein's rule, which states that no Al-O-Al links exist in a tetrahedral structure for an aluminosilicate, i.e.

$$(\text{Si/Al})_{\text{tet}} = \frac{I_{\text{Si(nAl)}}}{n/3 I_{\text{Si(nAl)}}}$$

it was estimated, from the deconvoluted (gaussian peaks) in Figures 1.2 (b) and (c), that the  $(\text{Si}/\text{Al})_{\text{tet}}$  ratio is  $11.5 \pm 1.0$ . (The assignment of the  $^{29}\text{Si}$  peaks at  $-88$  ppm and  $-93$  ppm to  $-\text{Si}(\text{OSi})_2(\text{OAl})$  and  $-\text{Si}(\text{OSi})_3$ , i.e. Si respectively is in agreement with the independent conclusions of Serratosa et al. who have examined the  $^{29}\text{Si}$  spectra of a range of micas).

- 5 It is concluded from the  $^{29}\text{Si}$  MASNMR spectra that the composition of the tetrahedral manifold is:

5

$$\text{Si}^{7.35 \pm 0.08} \text{Al}^{0.65 \pm 0.08}$$

a range which is compatible with the value of the layer charge ( $0.78 \pm 0.06$ ).

10

#### USE AS CATALYSTS

10

##### Example 10

- The  $\text{Al}^{3+}$ -exchanged form of the synthetic beidellite-smectite obtained in Example 1 was tested as a catalyst for the conversion of cyclohexylamine ( $\text{C}_6\text{H}_{11}\text{NH}_2$ ) to the secondary amine ( $\text{C}_6\text{H}_{11}\text{NHC}_6\text{H}_{11}$ ) under the conditions described in Example 32 of EP-A-31252.

15

The yield of the secondary amine was 24.9% (all percentages hereinafter are mole percents).

##### Example 11

- The  $\text{Al}^{3+}$ -exchanged form of the synthetic beidellitic-smectite obtained in Example 1 was tested as a catalyst in the formation of esters and isomers from hex-1-ene and acetic acid under the conditions described in Example 1 of EP-A-31252.

20

The yield of product was 12.0%. The ester product comprised hex-2-yl acetate (50.6%), hex-3-yl acetate (14.2%) and hexene isomers (35.2%).

##### Example 12

25

- The  $\text{Al}^{3+}$ -exchanged form of the synthetic beidellitic-smectite obtained in Example 1 was tested as a catalyst in the synthesis of ethers from n-pentanol under the conditions described in Example 17 of EP-A-31252.

- The yield of product was 42.0%. It comprised 1,1-dipentyl ether (56.8%), 1,2-dipentyl ether (4.8%) and pent-1-ene (38.4%).

30

##### Example 13

- Example 10 was repeated except that the  $\text{Al}^{3+}$ -exchanged form of the pillared beidellite-smectite of Example 10 was used in place of the beidellitic-smectite of Example 1.

- 35 The yield of secondary amine was 6.5%.

35

##### Example 14

- Example 11 was repeated except that the  $\text{Al}^{3+}$ -exchanged form of the pillared beidellitic-smectite of Example 9 was used in place of the beidellitic-smectite of Example 1.

- 40 The yield of product was 2.2%. It comprised hex-2-yl acetate (66.2%), hex-3-yl acetate (9.4%) and hexene isomers (24.4%).

40

##### Example 15

- Example 12 was repeated except that the  $\text{Al}^{3+}$ -exchanged form of the pillared beidellitic-smectite of Example 9 was used in place of the beidellitic-smectite of Example 1.

45

The yield of product was 6.3%. It comprised 1,1-dipentyl ether (60.5%), 1,2-dipentyl ether (3.8%) and pent-1-ene (35.7%).

##### Comparison Test 1

- 50 Example 10 was repeated except that the  $\text{Al}^{3+}$ -exchanged form of a standard, naturally occurring montmorillonite clay (Gelwhite, cf D.T.B. Tennakoon, W. Jones, J.M. Thomas, L.J. Williamson, J.A. Ballantine and J.H. Purnell, *Proc. Indian Acad. (Chem. Sci)*, 1983, 92, 27 for characterisation details) was used in place of the synthetic beidellitic-smectite.

50

The yield of the secondary amine was 27.9%.

55

##### Comparison Test 2

55

- Example 11 was repeated except that the  $\text{Al}^{3+}$ -exchanged montmorillonite as used in Comparison Test 1 was used in place of the synthetic beidellitic-smectite.

- 60 The yield of product was 34.1%. The composition of the product was hex-2-yl acetate (23.2%), hex-3-yl acetate (10.2%) and hexene isomers (66.6%).

60

*Comparison Test 3*

Example 12 was repeated except that the  $Al^{3+}$ -exchanged montmorillonite as used in Comparison Test 1 was used in place of the synthetic beidellitic-smectite.

The yield of product was 54.5%. It comprised 1,1-dipentyl ether (46.5%), 1,2-dipentyl ether (5.1%) and pent-1-ene (48.4%).

*Comparison Test 4*

Example 10 was repeated except that the  $Al^{3+}$ -exchanged form of the montmorillonite clay (as described in Comparison Test 1) pillared in an identical fashion to the beidellite of Example 9 was used in place of the  $Al^{3+}$ -exchanged beidellitic-smectite.

The yield of the secondary amine was 1.7%.

*Comparison Test 5*

Example 11 was repeated except that the  $Al^{3+}$ -exchanged form of the pillared montmorillonite as used in Comparison Test 4 was used in place of the  $Al^{3+}$ -exchanged synthetic beidellitic-smectite.

The yield of product was 0.3%, all of which was the hex-2-yl acetate.

*Comparison Test 6*

Example 12 was repeated except that the  $Al^{3+}$ -exchanged form of the pillared montmorillonite as used in Comparison Test 4 was used in place of the  $Al^{3+}$ -exchanged synthetic beidellitic-smectite.

The yield of product was 1.9%. The product composition was 1,1-dipentyl ether (63.9%), 1,2-dipentyl ether (28.0%) and pent-1-ene (8.1%).

Comparison Tests 1 to 6 are not examples according to the present invention and are included only for the purpose of comparison. It can be seen from the Examples and Comparison Tests that the synthetic beidellitic-smectite is similar in catalytic activity to the montmorillonitic-smectite, except for esterification in which its activity is significantly less. On the other hand, the pillared beidellite is significantly more active than the pillared montmorillonite for all the proton-catalysed reactions studied.

## CLAIMS

1. A synthetic beidellite-smectite having the idealised formula:



wherein  $M_{x/z}^{z+}$  represents exchangeable cations, and  $x$  represents the number of gram atoms of  $Si^{4+}$  replaced by  $Al^{3+}$  in the tetrahedral layers, and wherein  $x$  has a value of  $0.65 \pm 0.10$ .

2. A synthetic beidellitic-smectite according to claim 1 further characterised by a cation-exchange capacity of  $109 \pm 8$  meq per 100g of the dehydrated form, corresponding to a layer charge per formula unit of  $0.78 \pm 0.6$ .

3. A synthetic beidellitic-smectite according to either claim 1 or claim 2 further characterised in that the interlamellar distance is 10.0 Angstrom after dehydration at  $150^\circ C$  of the as-prepared magnesium-exchanged material ( $M^{2+}$  in the formula (I) =  $Mg^{2+}$ ).

4. A process for the production of a beidellitic-smectite as claimed in claims 1 to 3 which comprises hydrothermally crystallising an aqueous gel containing a source of silica, a source of alumina and a source of the exchangeable cation  $M^{2+}$  in a weight ratio of Si:Al:M of 7 to 8:3.5 to 5:0.5 to 1.

5. A process according to claim 4 which comprises the steps of:

(A) hydrolysing a hydrolysable aluminium compound,  
(B) adding a source of  $M^{2+}$  to the hydrolysate obtained in step (A) and homogenising the mixture so-obtained,  
(C) adding sodium hydroxide to precipitate a mixed hydroxide,  
(D) separating insoluble matter from the mixture obtained in step (B) and washing until substantially free from extraneous matter,

(E) re-dispersing in water insoluble matter separated in step (C),  
(F) adding a source of silica and homogenising the mixture, and  
(G) crystallising a beidellitic-smectite from the mixture of step (E).

6. A process according to claim 5 wherein the hydrolysable aluminium compound is an aluminium alkoxide.

7. A process according to either claim 5 or claim 6 wherein crystallisation is effected at a temperature in the range from 100 to  $350^\circ C$ .

8. A stabilised pillared analogue of the synthetic beidellitic-smectite as claimed in claims 1 to 3.

9. A process for producing the stabilised pillared analogue of a synthetic beidellitic-smectite as claimed in claim 8 which process comprises the process as claimed in United States Patent No. 4,176,090.



10. A process for producing the stabilised pillared analogue of a synthetic beidellitic-smectite as claimed in claim 8 which process comprises the process as claimed in United States Patent No. 4,248,739.
11. A process for producing the stabilised pillared analogue of a synthetic beidellitic-smectite as claimed in claim 8 which process comprises the process as claimed in United States Patent No. 4,238,364.
- 5 12. A process for producing a stabilised pillared analogue of the synthetic beidellitic-smectite as claimed in claim 8 which process comprises the process as claimed in United States Patent No. 4,216,188.
13. A process for producing the stabilised pillared analogue of a synthetic beidellitic-smectite as claimed in claim 8 which process comprises reacting under substantially anhydrous conditions in an organic solvent a synthetic beidellitic-smectite as claimed in claims 1 to 3 with a material capable of reacting with hydroxyl
- 10 groups associated with the structure of the smectite so as to interpose a residue of the material between adjacent layers of the smectite.
14. A process for carrying out a reaction capable of catalysis by protons wherein there is used as catalyst either a synthetic beidellitic-smectite as claimed in claims 1 to 3 or its stabilised pillared analogue as claimed in claim 8.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**